

COPOLYMERIZATION REACTIONS OF CARBON DIOXIDE

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ABSTRACT

Polymerization reactions of carbon dioxide were investigated with a view toward utilization of vast amounts as a chemical feedstock. Copolymerization of carbon dioxide with formaldehyde and paraformaldehyde in the presence of a variety of catalysts was investigated. In the presence of amine catalysts or Lewis acid catalysts, carbon dioxide copolymerizes with formaldehyde or paraformaldehyde to give a water-soluble polymer of polycarbonate structure. A 1:1 alternating copolymer is proposed from its infrared spectra showing a strong ester band at 1750 cm^{-1} . From high-pressure liquid chromatography analysis, number-averaged molecular weight was determined to be about 20,000. However, mixing in 25% of a comonomer spacer (ethylene glycol) gave a polymer with twice the molecular weight. The addition of boric acid resulted in cross-linking of the polymer and a significant increase in the viscosity of the aqueous solution.

INTRODUCTION

Since 1969 when Inoue and coworkers (1, 2) first reported the synthesis of high-molecular-weight poly(propylene carbonate) by copolymerization of CO_2 and propylene oxide using organozinc catalysts, copolymerization of carbon dioxide has been widely studied (3). Because of the low cost and accessibility of the monomers and the attractive properties of polycarbonates, there has been considerable recent interest in the development of catalysts for the alternating copolymerization of carbon dioxide with epoxides (3-7). Recently, Chiang (8) reported copolymerization of carbon dioxide and formaldehyde to give a 1:1 alternating copolymer. The nature of the product from alternating copolymerization of CO_2 with carbonyl compounds in the presence of a variety of acid and base catalysts is reported here.

EXPERIMENTAL

Reactions were conducted in a 300-mL pressurized Parr autoclave with generally 16 g of CO_2 and an equimolar amount of aldehyde equivalent with 5% by weight of catalyst. Products were worked up differently depending on the solvent for the reaction. In a typical run, a mixture of aqueous formaldehyde (37%), catalyst, and dry ice was placed in a 300-mL Parr reactor. The reactor was sealed under nitrogen and heated at the desired temperature for the desired time period. The reaction products were soluble in the water solvent used for the reaction. For the reactions of paraformaldehyde and trioxane, methyl *tertiary* butyl ether (MTBE) or dioxane were used as solvents.

Polymer products were analyzed by infrared (IR) spectroscopy and gel permeation chromatography (GPC). Aqueous solutions of the polymeric products were analyzed with high-pressure GPC on a TSK30 gel column with water eluent and ultraviolet (UV) detection at 210 nm, and dioxane solutions were analyzed with a mixed pore size photoluminescence gel column in tetrahydrofuran (THF) solvent. Molecular weights (M_w) were calibrated using retention times of proteins and polymer standards with narrow M_w distributions. Reaction yields were also determined on the GPC column. The copolycarbonate peak area was calibrated using a known concentration of a standard consisting of a purified copolycarbonate sample.

RESULTS AND DISCUSSION

Base Catalysis

A comparison of the catalytic effects of a series of organic bases was conducted on the reactions of carbon dioxide with aqueous formaldehyde to form the acetal copolycarbonate ester (Figure 1). The reactions were performed in a pressurized autoclave at 120°C using organic bases, triethylamine (TEA), dimethylaminopyridine (DMAP), and diazabicyclooctane (DABCO) as catalysts for the reactions (Table 1). Chiang used TEA as the catalyst (8). The DMAP and DABCO are much more basic and were expected to exert a better catalytic effect.

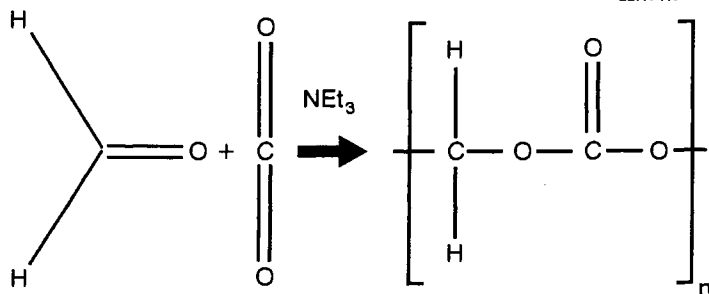


Figure 1. Acetal copolycarbonate formation.

TABLE I

Reactions of Formaldehyde							
Aldehyde	Catalyst	Solvent	Temp., °C	Time, hr	Polymer	Solubility	M _w (yield)
HCHO (37%, 40 mL)	TEA (2 g)	Water	120	100	Very viscous oil (4.01 g)	Somewhat soluble in water	23,000 (1%) 20,000 (17%) 16,000 (19%) 12,000 (8%)
HCHO (37%, 40 mL)	DMAP (2.3 g)	Water	120	100	Very viscous oil (6.2 g)	Somewhat soluble in water	22,000 (8%) 14,000 (27%) 11,500 (15%) 1000 (20%) <1000 (rest)
HCHO (37%, 40 mL)	DABCO (2.24 g)	Water	120	100	Very viscous oil (5.1 g)	Somewhat soluble in water	22,000 (22%) 1000 (17%) <1000 (rest)

* HCHO = formaldehyde.

The product from aqueous formaldehyde reaction was water-soluble. Extraction of the product with ether recovered about 70% of the base catalyst. The amount of the acetal polycarbonate was determined by GPC. Polymer peaks eluted early, and molecular weights and amounts were determined from retention times and peak areas. Low-molecular-weight oligomers were also present in the products, as evidenced by the presence of a late GPC peak. The results in Table I show that higher yields of polymer were obtained from the reaction using the more powerful base DMAP. TEA gave the lowest yield and is the most volatile.

Water was removed from the reaction products by low-vacuum distillation. The impure reaction products were tacky solids with good water and ethanol solubility, but poor solubility in THF and dioxane. IR spectroscopy of the products indicated that substantial amounts of aliphatic ester carbonyl groups were present, verifying that the desired incorporation of CO₂ to form the polycarbonate ester had occurred.

A comparison of the reaction conditions was also performed for the reaction in aqueous formaldehyde using the basic catalyst, DMAP. This reaction matrix varied temperature (120° to 200°C) and the reaction time (12 versus 24 hr). Relevant data are given in Table 2. For the 12-hr series of runs, polycarbonate yields increased with temperature as follows: 120°C, 4%; 150°C, 5%; 175°C, 9%; 200°C, 11%. Increasing the reaction time to 24 hours at 150°C increased the yield from 5% to 7%. The molecular weight of the polymer products was about 20,000 daltons for most of the reactions, but was 40,000 for the reaction at 175°C.

Two disadvantages of the aqueous formaldehyde became obvious during these initial studies: 1) the product polymers are not easily separated from the reactant formaldehyde and oligomers, owing to similarity in solubility and difficulty in distilling the formaldehyde off without decomposition; 2) the aqueous formaldehyde contains methanol (normally 5%–15% present in commercial formalin solution) that could cap the ends of the chains as an acetal linkage. Methanol and formic acid are also formed as byproducts in the reaction via the Cannizzaro reaction of aldehydes in base. Although it is displaceable from the end formaldehyde unit, it would inhibit the reaction and prevent the reaction with the CO₂.

TABLE 2

Reactions of Aqueous Formaldehyde							
Aldehyde	Catalyst	Solvent	Temp, °C	Time, hr	Polymer	Solubility	M _w (yield)
Formaldehyde (40 mL, 37%) + Ammonium Carbonate (42 g)	DMAP (2.37 g)	Water	120	24	Orange solution (1.21 g)*	Water	20,000 (58%) 19,500 (42%)
Formaldehyde (40 mL, 37%) + Dry Ice (16 g)	DMAP (2.37 g)	Water	120	24	Orange solution (1.21 g)*	Water	20,000 (58%) 19,500 (42%)
Formaldehyde (40 mL, 37%) + Dry Ice (16 g)	DMAP (2.37 g)	Water	150	12	Orange solution (1.63 g)*	Water	85,000 (2%) 20,000 (98%)
Formaldehyde (40 mL, 37%) + Dry Ice (16 g)	DMAP (2.37 g)	Water	150	24	Orange solution (2.24 g)*	Water	16,000 (51%) 15,500 (49%)
Formaldehyde (40 mL, 37%) + Dry Ice (16 g)	DMAP (2.37 g)	Water	175	12	Orange solution (2.84 g)*	Water	40,000 (100%)
Formaldehyde (40 mL, 37%) + Dry Ice (16 g)	DMAP (2.37 g)	Water	200	12	Orange solution (3.1 g)*	Water	21,000 (48%) 20,000 (52%)

* Yield based on GPC data.

Paraformaldehyde Reactions

An investigation of the reactions of paraformaldehyde with CO₂ was conducted in ether and ester solvents at 120°C (see Table 3). The products were compared for reactions with two basic catalysts, DMAP and DABCO, in two solvents, MTBE and dioxane. The molecular weights of the products were determined by high-pressure GPC. In MTBE solvent, the stronger of the base catalysts, DMAP, resulted in the highest yields of polycarbonate, but the molecular weight of the product (12,000) was lower than that obtained with DABCO (19,000 and 23,000, two peaks). Yields in dioxane were similar for the two bases. Reactions in the ester solvent (ethyl acetate) gave no polymer product. The reaction products had limited solubility in dioxane, so were easily separated as a viscous liquid by decantation of the solvent. This product exhibited high water and ethanol solubility. IR spectroscopy confirmed its polycarbonate structure.

TABLE 3

Reactions of Paraformaldehyde							
Aldehyde	Catalyst	Solvent	Temp., °C	Time, hr	Polymer	Solubility	M _w (yield)
Paraformaldehyde (15 g) + Dry Ice (16 g)	DMAP (2.37 g)	Dioxane (40 mL)	120	48	Viscous oil (6.5 g)	Water	85,000 (16%) 23,000 (48%) 22,000 (37%)
Paraformaldehyde (15 g) + Dry Ice (16 g)	DMAP (2.37 g)	Dioxane (40 mL)	120	24	—	—	—
Paraformaldehyde (15 g) + Dry Ice (16 g)	DABCO (3.58 g)	Dioxane (40 mL)	120	24	Viscous oil (3.5 g)	Water	—
Paraformaldehyde (15 g) + Dry Ice (16 g)	DMAP (2.3 g)	Dioxane (30 mL)	175	12	Viscous oil (10.33 g)	Water	23,000 (100%)
Paraformaldehyde (22 g) + Dry Ice (24 g)	None	Dioxane (40 mL)	120	24	—	—	—
Paraformaldehyde (15 g) + Ethanolamine (30.5 g) + Dry Ice (16 g)	DABCO (2.3 g)	Dioxane (40 mL)	120	24	Viscous oil (51 g)	Water	<1000 (86%) 19,000 (12%) 45,000 (1%)

Higher-temperature reactions of paraformaldehyde were also investigated. Reactions of paraformaldehyde with CO₂ in dioxane solvent (DMAP catalyst) at 175°C for 12 hr gave a 33% yield compared with a yield of 21% for the reaction at 120°C for 48 hr. The molecular weights were

similar for the two reactions (23,000). Thus temperature has a very significant effect in increasing the reaction yields, but does not significantly affect the molecular weights.

Paraformaldehyde gave higher yields of polymer than aqueous formaldehyde. The reaction of paraformaldehyde required the catalyzed depolymerization to the reactive monomer *in situ*. When paraformaldehyde was heated in dioxane at 120°C for 24 hr, no formaldehyde was formed. However, when paraformaldehyde was heated in dioxane in the presence of 4-dimethylaminopyridine, a significant amount of formaldehyde was formed. Quantitative analysis was not performed. Trioxane does not decompose to formaldehyde in base and therefore did not react to form polymer.

Reactions of Trioxane

Trioxane, the trimer of formaldehyde, is easily formed from formaldehyde and represents a soluble form. One reaction of trioxane was attempted with CO₂ with the DMAP catalyst at 150°C. No polymer formed in the reaction. The basic catalyst was not effective in breaking down the trioxane to formaldehyde for the copolymerization.

Reactions with Glycol Comonomer

Incorporation of ethylene glycol as a comonomer was attempted to determine if additional stability would result from the presence of the glycol or 1,2-dioxy unit in the chain. This unit would be expected to be more stable than the vicinal acetal or 1,1-dioxy unit that results from polymerization of the aldehydes. Thus, the polymerization of CO₂ with paraformaldehyde and 25% ethylene glycol in a dioxane solvent and DABCO catalyst was carried out. The ethylene glycol unit was also expected to modify the crystallinity of the chains by acting as a "spacer" group.

The copolymer products obtained with ethylene glycol contained 58% of a significantly higher-molecular-weight polymer (42,500 daltons) in addition to the normal 20,000-dalton polymer. The products were still soluble in water. Further reactions with epoxide and other comonomer mixtures are needed to understand and optimize the copolymerization reaction chemistry.

Copolymerization of Other Aldehydes

The scope of the acetal copolycarbonate reaction was expanded to include other aldehydes. Reactions of acetaldehyde were conducted with carbon dioxide in dioxane (DMAP catalyst) at 150°C (see Table 4). A low yield of polymer was obtained. The condensation product, crotonaldehyde, and low-molecular-weight oligomers were present. A repetition at this temperature gave similar results. A reaction temperature of 175°C gave higher yields than the reactions at 150°C. In contrast to the formaldehyde copolycarbonates, the polymer products from the acetaldehyde polymerization were not water-soluble. The acetaldehyde copolycarbonate is in fact soluble in dioxane and THF. The molecular weight of the product from the higher-temperature reaction (19,000) was similar to that from the 150°C reaction. With the basic catalyst, the major products result from condensation rather than copolymerization. Reactions of a second aldehyde (furfuraldehyde) with CO₂ were also investigated at 120°C. The product was, however, only partially soluble and appeared to have been converted to a pitch under the reaction conditions.

TABLE 4

Reactions of Acetaldehyde							
Aldehyde	Catalyst	Solvent	Temp., °C	Time, hr	Polymer	Solubility	M _w (yield)
Acetaldehyde (22 g) + Dry Ice (16 g)	DMAP (2.37 g)	Dioxane (40 mL)	150	12	(0.73 g)*	Dioxane	86,000 (35%) 20,000 (97%)
Acetaldehyde (22) + Dry Ice (16 g)	DMAP (2.3 g)	Dioxane (40 mL)	175	12	(5.73 g)*	Dioxane	19,000 (100%)

* Yield based on GPC data.

Lewis Acid Catalysis

A large number of Lewis acid catalysts have been tested in other laboratories for the related copolymerization of epoxides with CO₂ (2-7). One of these catalysts, zinc bisanil (7), was prepared for the reactions of CO₂ with paraformaldehyde and acetaldehyde. The function of the acid catalyst is to break down the paraformaldehyde or trioxane, as well as catalyze the copolymerization.

Several forms of the Zn bisanil catalyst were investigated. The methoxide form gave a white polymeric film on top of an orange solution. The polymeric film was separated by filtration. The white film was air-dried and weighed. The orange solution was evaporated to remove solvent. Upon removal of solvent, a highly viscous orange oil was formed. The oil was completely soluble in water and was analyzed by GPC. Relevant data are given in Table 5.

TABLE 5

Zinc Bisanil Complex-Catalyzed Reactions of Paraformaldehyde and CO₂

Aldehyde	Catalyst	Solvent	Temp., °C	Time, hr	Polymer	Solubility	M _w (yield)
Paraformaldehyde (15 g)	Bisanil + NaOMe +ZnCl ₂ (1.08 g)	Dioxane (40 mL)	150	20	Orange oil (8.71 g) White solid	Water	21,500 (18%) 18,000 (6%) 1000 (52%) <1000 (rest)
Paraformaldehyde (15 g)	Bisanil ZnCl ₂ (3.54 g)	Dioxane (40 mL)	150	12	Orange oil (4.62 g)	Water	
Paraformaldehyde (15 g)	Bisanil ZnTCA (0.5 g)	Dioxane (40 mL)	150	12	Orange oil (6.26 g)	Water	85,000 (1.5%) 24,000 (3%) 21,000 (36%) 17,000 (24%) 13,000 (7%)

The methoxide form of the catalyst gave the most product, but only a portion of it was the 21,000-dalton polymer. Most was the oligomers. The chloride form gave the least product, and since it was not soluble in water, it has not yet been analyzed in the GPC system. The trichloroacetate form was reasonably successful in producing the 17,000- to 21,000-dalton product.

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CARBON DIOXIDE CATALYSIS IN TRANS-ESTERIFICATION REACTION FOR THE CARBAMATION OF AMINES OF INDUSTRIAL INTEREST

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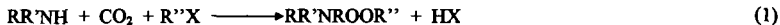
Abstract: Developing clean synthetic methodology for the production of carbamates, avoiding phosgene, is a very attractive perspective. In this paper, the reactivity of industrially relevant amines, aliphatic and aromatic, towards CO₂ and alkylating agents, or dialkyl/aryl-carbonates, is discussed. We also describe the catalytic role of carbon dioxide in the carbamation of aliphatic amines and that of P-acids in the reaction of aromatic amines towards carbonates. The reaction mechanism is discussed.

Keywords: carbon dioxide, organic carbamates, amines.

Introduction

Organic carbamates are compounds of great interest used in pharmacology, agriculture, and chemical industry.¹ Their conventional syntheses are based on the use of phosgene, a chemical difficult to handle because of its toxicity. The substitution of phosgene with less noxious starting materials represents a very important target of "green chemistry" for the future. Carbon dioxide and organic carbonates are good candidates as succedaneous for phosgene.²

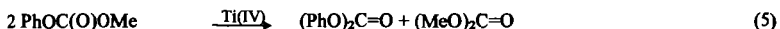
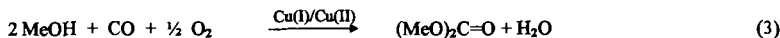
Utilisation of carbon dioxide in the synthesis of carbonate esters has been investigated for long time. We have reported about their selective synthesis from amines, CO₂ and alkylating agents³ [Eq. 1]:



Aminolysis of organic carbonates [Eq. 2] is another attractive synthetic route to carbamates, since non-phosgene routes to carbonic acid diesters are now available.



In fact, dimethylcarbonate (DMC) is produced on large-scale by oxidative carbonylation of methanol [Eq. 3], and other organic carbonates can be prepared by transesterification of DMC with phenols or long chain alcohols [Eq. 4, 5]



Carboalkoxylation of aliphatic amines requires suitable catalysts in order to observe high conversion rate and good selectivity. Lewis acids, such as AlCl₃, SnCl₂, ZnCl₂, FeCl₃, or metal (Rh, Ru) complexes, can catalytically promote the carboalkoxylation of aliphatic amines with carbonates. A major drawback is the methylation of the amine.

Recently, we have shown that carbon dioxide is an efficient catalyst for the synthesis of organic carbonates from aliphatic amines and DMC.⁴ As this synthetic approach requires mild conditions, we have extended our studies to aminofunctional silanes. The corresponding carbamates are used as modulators of physico-mechanical properties of polymeric materials.⁵ CO₂ plays again a quite interesting catalytic role.

The conventional carboalkoxylation/arylation of aromatic amines, obtained using Zn, Co, Sn, Al, Ti catalyst, has again as major drawback the alkylation/arylation of the amines. We have found that in this case organophosphorous acids can be advantageously used as very selective catalysts avoiding the alkylation/arylation process.

Experimental

All reaction and manipulation were carried out under the specified atmosphere, by using vacuum line techniques. All solvents were dried as described in literature⁶, and they were stored under dinitrogen.

Synthesis of RNHC(O)OCH₃ from aliphatic amines or aminofunctional silanes and DMC in the presence of CO₂

A solution of amine (9.15 · 10⁻³ mmol) in DMC (10 mL) was prepared under dinitrogen in an appropriate flask and, then, saturated with CO₂ (P_{CO₂} = 0.1 MPa) to give (RCH₂)₃NH₃⁺·O₂CNH(CH₂R) as white microcrystalline solid which was poorly soluble in the reaction solvent. The system was heated to 343 K for 5-7 h. After cooling to room temperatures

the reaction mixture was filtered. A small amount of unreacted $(\text{RCH}_2)_3\text{NH}_3^+\text{O}_2\text{CNH}(\text{CH}_2\text{R})$ was recovered. The solution was evaporated in vacuo and the residue fractionated on a silica gel column using a diethyl ether/hexane (2:1 v/v) eluent mixture. Solvent was evaporated from the eluted fractions and pure carbamate obtained.

When the reaction mixture was heated at 363 K, an increase of the yield (Table 1) was observed.

Table 1. Yield of carbamate esters from aliphatic amines or aminofunctional silanes and DMC in the presence of carbon dioxide

Amine	Yield (%)	Yield (%)
$(\text{PhCH}_2)_3\text{NH}_2$	50 (343 K)	92 (363 K)
$\text{C}_6\text{H}_{11}\text{NH}_2$	27 (343 K)	45 (363 K)
$\text{CH}_2=\text{CHCH}_2\text{NH}_2$	44 (343 K)	70 (363 K)
$\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$	70-80 (348 K)	/
$\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$	70-80 (348 K)	/
$\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$	100 (348 K)	/

Synthesis of mono- and di-carbamates, from aromatic di-amines and 1) diphenylcarbonate (DPC) or 2) methylphenylcarbonate (MPC), in the presence of phosphorous acids

1) A mixture of DPC (26.1 mmol), di-amine (1.35 mmol) and phosphorous acid (0.135 mmol) was heated at 363 K under stirring for 4 h. The mixture was cooled to room temperature (293 K) and the solid was extracted with diethyl ether. The white residue was analysed as pure di-carbamate. By reducing the reaction time to 30 min, it was possible to isolate the mono-carbamate (Table 2) by using the same purification procedure.

2) A mixture of MPC (6.9 mmol), di-amine (3.45 mmol) and phosphorous acid (0.347 mmol) in THF (10 mL) was stirred at 363 K for 10 h, then cooled to room temperature and the solid that precipitated was isolated by filtration and identified as $(\text{ArH}_2)(\text{O}_2\text{PPh}_2)_2$. The solution was fractionated on a silica gel column using diethyl ether/toluene for MDA and diethyl ether/hexane for TDA as eluent. Methylphenylcarbonate afforded very selectively the methylcarbamate without production of neither phenyl carbamate nor methyl-amine.

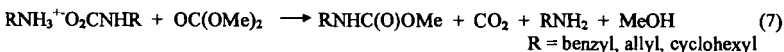
Table 2. Yield of mono- and di-carbamate synthesised from di-amines and carbonates in the presence of phosphorous acids.

Di-amine	Yield (%) of Mono-carbamate	Yield (%) of Di-carbamate	Phosphorous acid
$\text{H}_2\text{NPh}(\text{CH}_2)_2\text{PhNH}_2$	50 (DPC)	100 (DPC)	$\text{Ph}_2\text{P}(\text{O})\text{OH}$
$\text{H}_2\text{NPh}(\text{CH}_2)_2\text{PhNH}_2$	35 (MPC)	32 (MPC)	$\text{Ph}_2\text{P}(\text{O})\text{OH}$
$\text{H}_2\text{NPh}(\text{CH}_3)_2\text{NH}_2$	42 (DPC)	84 (DPC)	$\text{Ph}_2\text{P}(\text{O})\text{OH}$
$\text{H}_2\text{NPh}(\text{CH}_3)_2\text{NH}_2$	51 (MPC)	66 (MPC)	$\text{Ph}_2\text{P}(\text{O})\text{OH}$

Results

Reactivity of aliphatic amines towards DMC in the presence of carbon dioxide

Saturation of an amine solution in DMC with carbon dioxide gives the corresponding alkylammonium N-alkylcarbamate that reacts with DMC to afford N-alkylmethylcarbamates [Eq. 6, 7].



The alkylammonium N-alkylcarbamate was prepared *in situ* and, after its precipitation, the reaction mixture was heated to the required temperature. The reaction was carried out in conventional solvents as THF, CH_2Cl_2 , and aromatics. Interestingly, the organic carbonate (DMC) could be used as reaction solvent. In order to ameliorate the reaction rate and selectivity, we have tested different reaction conditions and established that working at temperature higher than 343 K and pressure of $\text{CO}_2 = 0.1 - 0.2$ MPa produces best results. In all cases, the products have been completely characterised. By-products as ureas, N,N-substituted carbamates, secondary and tertiary amines were formed in very low yield (< 1%), if not absent. Conversely, if aliphatic amines were reacted with DMC under N_2 atmosphere the formation of carbamate esters was completely suppressed and methylation products were formed.

Reactivity of aminofunctional silanes towards DMC in the presence of carbon dioxide

Under mild condition (348 K), aminofunctional silanes as $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$ (I), $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ (II), $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$ (III) react with DMC in the presence of carbon dioxide to give the corresponding carbamate esters $\text{MeO}(\text{O})\text{CNH}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$, $\text{MeO}(\text{O})\text{CNH}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$, $\text{MeO}(\text{O})\text{CNH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$, respectively.

The carbamation reaction is very selective⁷; no formation of N-mono- or N,N'-di-methylated derivatives as by-products has been observed.

The reactivity of the di-amine (III) was higher than that of amines (I) and (II). In fact, the conversion of (III) into the corresponding carbamate was complete in less than 7 hours.

When the reactivity of silyl amines towards DMC, at 348 K, was investigated in a dinitrogen atmosphere the carbamation reaction was not observed: the formation of N-methylated species was the main process.

The development of new clean methodologies for these products is required by the fact that silyl carbamates are more and more used as silane coupling agents and as source of isocyanates, largely used in the chemical industry.

Reactivity of 4,4'-methylenedianiline (MDA) and 2,4-diaminotoluene (TDA) towards DPC or MPC in the presence of P-acids

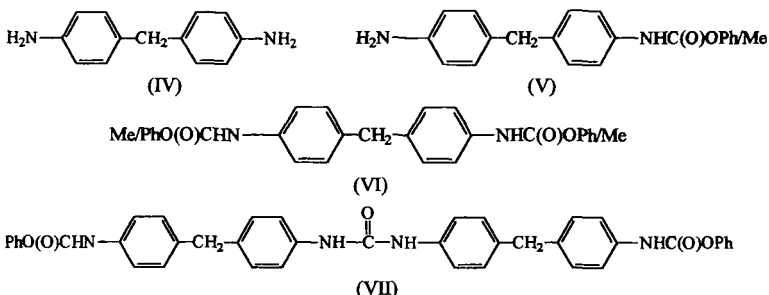
Aromatic amines show a poorer reactivity towards DPC or MPC in the presence of CO₂ with respect to aliphatic ones. This behaviour is most probably due to their low nucleophilicity. In the presence of catalysts such as Ph₂P(O)OH, (PhO)₂P(O)OH, (BuO)₂P(O)OH, (BuO)P(O)(OH)₂ aromatic mono-⁸ and di-amines^{9,10} react with DPC and DMC to give the corresponding carbamate esters with high yield and selectivity. DPC affords the phenyl carbamate, while MPC¹⁰ affords selectively the methyl carbamate and results to be a much better carboxymethylating agent than DMC.

In order to gather information about the reaction mechanism of mono- and di-carbamate of MDA (IV) with either DPC or MPC, we have carried out a kinetic study. At 363 K, mono-carbamate (V) was formed followed by di-carbamate (VI), in very good yield. In absence of the catalyst, no reaction was observed. The kinetics is first order in the amine and first order in the carbamate.¹¹

Carrying out the reaction in THF as solvent, at different temperatures (393, 363, 323 K) it was possible to establish the better reaction conditions for addressing the reaction towards the preferential formation of mono- or di-carbamate.

The temperature affects the selectivity of the reaction. In fact at 393 K, when DPC is used, the formation of urea (VII) is observed, produced by reaction of the di-carbamate with mono-carbamate. At 363 K, urea is not observed.

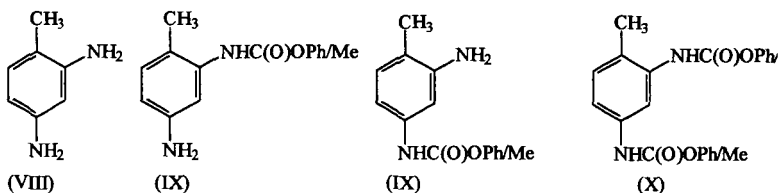
Interestingly, when MPC¹⁰ was used, urea was never detected.



The carbamation reaction was studied using solvents as diethyl ether, phenol or the carbonate itself. The use of phenol as solvent produces an inhibitory effect on the carbamation process, that results to be very selective when the carbonate is used as solvent. The conversion of the amine is quantitative.

The P-acids used as catalyst have shown a quite different activity, Ph₂P(O)OH being the most active. In the case of MPC a progressive deactivation of the catalyst was observed after sixteen hours. Further addition of catalyst results, in fact, in a significant increase of the rate of formation of both carbamates.

The P-acids show a very interesting catalytic activity also in the carbamation process of TDA (VIII). The formation of mono- (IX) and di-carbamate (X) is observed with high yield and selectivity.



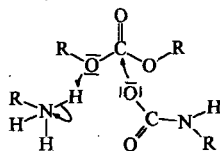
The formation of (X) involves the carbamation of two non-equivalent amino groups of the aromatic di-amine. We have demonstrated that the amino group in the *para* position is functionalised first than that in *ortho*. This is due to the hindrance of the methyl group that induces the faster reactivity of the amino group in the *para* position.

MDA and TDA carbamates have a large market as they are used as precursors of isocyanates, which are monomers for polymers.

Discussion

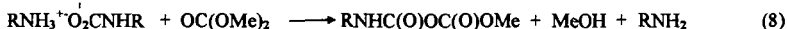
Carbon dioxide as catalyst

The results reported above, and the experiments carried out in absence and in presence of CO₂, clearly demonstrate that carbon dioxide plays a catalytic role in the carbamation of aliphatic amines. The kinetic study we have completed¹¹ shows that the rate determining step is the reaction of carbamate anion with the carbonate [Eq. 8], that bears to the formation of the mixed carbamic-carbonic anhydride RNHC(O)OC(O)OMe. Scheme 1 shows the reactive step.



Scheme 1.

Subsequently it is decarboxylated to form the carbamate ester.

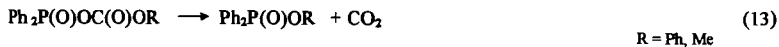
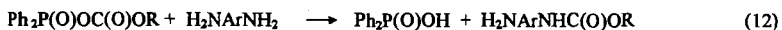
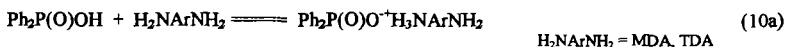


The mixed anhydride has been isolated and characterised. It is stable at low temperature and at room temperature, or higher, spontaneously converts into the carbamate with CO₂ loss. This mechanism explains why the incorporation of labelled CO₂ in the organic carbamate is not observed when RNH₃⁺O₂¹³CNHR is utilised as the starting reactant.

The reaction conditions are quite mild and selectivity is 100%.

Role of the P-acids in the carbamation process

Aromatic amines show a lower reactivity towards carbon dioxide, so the carboalkoxylation process requires suitable catalysts. Phosphorous acid can be considered as bifunctional catalysts. A plausible mechanism involves the formation of a carbonic-diphenylphosphinic mixed anhydride Ph₂P(O)OC(O)OPh, that reacts with the free aromatic amines which are converted into the carbamate esters, with regeneration of the catalyst.



R = Ph, Me

The catalyst is still active at the end of the several runs if the process involves DPC. MPC can cause a progressive deactivation of the catalyst.

This could be explained considering that in the former case the starting catalyst may be converted into Ph₂P(O)OPh, that is also a catalytic species. In the latter, the catalyst converts into Ph₂P(O)OMe that has no catalytic properties.

Conclusion

In the presence of carbon dioxide, aliphatic amines and aminofunctional silanes react with carbonates (DMC) to give the corresponding carbamate esters. The carbon dioxide catalysis is a new, useful finding. The selectivity is very high.

This methodology cannot be extended to the carboalkoxylation of aromatic amines, most probably because they show a lower reactivity towards CO₂. Aromatic amines and carbonate can be converted into the corresponding carbamate esters in the presence of P-acids as catalyst.

In both cases, the carbamation reaction is very selective and no formation of N-methyl/aryl species or ureas is observed.

Acknowledgements

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CAMERE PROCESS FOR CARBON DIOXIDE HYDROGENATION TO FORM METHANOL

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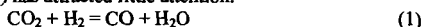
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KEYWORDS: CAMERE process, methanol, CO₂ hydrogenation

INTRODUCTION

Catalytic hydrogenation of CO₂ has been one of major approaches to diminish the greenhouse gas because large amounts of CO₂ can be converted to resources such as methanol and other oxygenates compounds by the reaction. However, a direct hydrogenation of CO₂ shows low conversion, which increases the recycle gas to obtain high methanol productivity. CAMERE process (Scheme 1) has been developed to form methanol from CO₂ via a reverse-water-gas-shift reaction (1). In the CAMERE process, carbon dioxide is converted to CO and H₂O by the reverse-water-gas-shift reaction (RWReaction) and then, the produced gas (CO/CO₂/H₂) is fed to the methanol reactor after removing the water. Each reactor in the process has the recycle stream to increase CO₂ conversion to CO and carbon oxide (CO₂+CO) conversion to methanol, respectively. With the gas feeding of CO/CO₂/H₂, the water produced in the methanol reactor is chemically eliminated through a water-gas-shift reaction, increasing carbon oxide conversion to methanol and then decreasing the recycle gas in the methanol reactor. The methanol productivity in the CAMERE process depends on the CO concentration in the feed gas of the methanol reactor, which is dependent on the RWReaction conditions, especially the temperature.

A water-gas-shift reaction has been studied intensively for the last several decades in order to adjust for H₂/CO ratio in the synthesis gas (2-4). On the contrary, a reverse- water-gas-shift reaction of Eq.(1) has attracted little attention.



Besides, all the kinetic equations published on the RWReaction have been obtained over copper-containing catalysts at low temperatures (5-7). Therefore, we need to develop a mathematical model for the RWReaction at high temperature to predict the effects of operating condition changes of the RWReactor on the overall performance of the CAMERE process. A mathematical form based on a redox mechanism is obtained over Fe₂O₃/Cr₂O₃ catalyst at 773 K. Apparent activation energy for the RWReaction is calculated from an arrhenius plot of specific activities acquired over the temperature of 673-823 K, which is 109.8 kJ/mol. The CAMERE process has been evaluated based on the kinetic equation of the RWReaction to find an optimum operating condition to form methanol from CO₂.

EXPERIMENTAL

A commercial Fe₂O₃/Cr₂O₃(Fe:Cr=9:1 in molar ratio) catalyst was investigated to obtain a kinetic equation for the RWReaction over the temperature of 593-723 K. The catalyst charged in a tubular catalytic reactor is heated up to a reaction temperature in the presence of CO₂ and H₂ before the RWReaction. The RWReactions are performed under the reaction conditions of 1atm, temperature of 670-823 K, and W/F (g_{cat}.h/mol of CO₂ in the feed) of 0.05-3.7. The absence of diffusion limitations is confirmed by changing the size and the amount of the catalyst.

RESULTS AND DISCUSSION

The RWReaction is endothermic, and hence conversion of CO₂ is favored by high reaction temperature. Hence the RWReaction should be operated at high temperature above 773 K to keep CO₂ conversion up to 60%, increasing carbon oxide conversion to methanol in the second step of the CAMERE process. The kinetic studies for the RWReaction are performed in an integral plug flow reactor over Fe₂O₃/Cr₂O₃ catalyst at 773 K. A redox mechanism is derived from the best fitting of the experimental data. The surface of the Fe₂O₃/Cr₂O₃ catalyst is successively oxidized by CO₂ and reduced by H₂ by the redox mechanism. For the redox mechanism a rate expression is derived from that the step, which the catalyst surface was reduced by H₂, is a rate-determining step. The kinetic equation is expressed as follows;

$$r = \frac{P_{\text{CO}_2} P_{\text{H}_2} / P_{\text{CO}} - P_{\text{H}_2\text{O}} / K}{1/kK_1 + P_{\text{CO}_2}/kP_{\text{CO}}}$$

where, k = apparent rate constant of the RWReaction (mol h⁻¹ g_{cat}⁻¹ atm⁻¹)

K = equilibrium constant of the RWReaction (dimensionless)

K_1 = equilibrium constant of the surface oxidation step by CO₂ (dimensionless)

r = reaction rate (mol h⁻¹ g_{cat}⁻¹), P_i = partial pressure of i component (atm)

Overall apparent activation energy can be determined from the effect of temperature on the rate for the RWReaction at a constant composition. Hence the RWReaction is performed with

temperature over the W/F ($g_{cat}/h/mol$ of CO_2 in the feed) of 0.05-1.5. Figure 1 gives the experimental data and the values calculated from the kinetic equation for the RWReaction. An arrhenius type plot of $\ln(\text{rate})$ versus $1/T$ is obtained from CO_2 conversion with the reaction temperature. Figure 2 shows the activation energy of 109.77 kJ/mol for the RWReaction. The activation energy is similar to that of copper-containing catalyst (8).

The CAMERE process has been simulated based on the kinetic equation of the RWReaction and carbon oxide conversion to methanol to compare the operating conditions of the CAMERE process with those of a direct CO_2 hydrogenation. We use the published results on the carbon oxide conversion to methanol under the reaction conditions of 50 atm and 523 K (9-10). Table 1 shows the simulation results that are dependent on the presence and conditions of the RWReaction. The same amount (14.3 kgmol/hr) of CO_2 and H_2 is fed to the direct CO_2 hydrogenation and CAMERE process, respectively. In the methanol reactor the recycle gas is calculated by subtracting the purge gas (=P) from the downstream gas (=F2). To obtain methanol productivity of 2 kg mol/h, the gas of 42.82 kgmol/h should be recycled in the direct CO_2 hydrogenation process. On the other hand, the gas of 16.27 kgmol/h is recycled in the CAMERE process to form methanol of 2.06 kgmol/h where there is no recycle step in the RWReactor ($R1=0$). Moreover, the recycle gas is further reduced to 10.66 kgmol/h when the recycle ratio is the one in the RWReactor ($R1=1$). It means that the recycle gas for the same methanol production strongly depends on the CO concentration in the feed gas of the methanol reactor (F1). The CO concentration is decided by the presence of the RWReaction and the recycle ratio ($R1$). The CO concentration in the F1 stream increases when the temperature and recycle ratio of the RWReaction is increased. With the elimination of water by the RWReaction, the recycle gas of the CAMERE process is minimized compared with the direct CO_2 hydrogenation process to form the same amount of methanol. Therefore, the reactor size to obtain methanol of 2 kgmol/h in the CAMERE process can be decreased up to one fourth of the one of the direct CO_2 hydrogenation process when the product gas of 50% in the RWReactor is recycled. Table 1 indicates the relationships between CO concentrations in the feed gas with the recycle gas for the same methanol production. The water produced in direct CO_2 hydrogenation process is comparable with that in the methanol reactor of the CAMERE process, that are 2.31 kgmol/h in the direct process and 0.34 kgmol/h in the CAMERE process ($R1=1$) for the same methanol production of 2.0 kgmol/h, respectively. The pilot plant for methanol production of 5 kg/day is constructed in our laboratory.

CONCLUSIONS

A rate equation for a reverse-water-gas-shift reaction is obtained based on a redox mechanism over Fe_2O_3/Cr_2O_3 catalyst at 773 K, which apparent activation energy is 109.8 kJ/mol. The CAMERE process has been simulated based on the kinetic equation of the RWReaction and carbon oxide conversion to methanol to find an optimum operating conditions to form methanol from CO_2 . With the elimination of water by the RWReaction, the recycled gas in the CAMERE process is decreased more than four times compared with a direct CO_2 hydrogenation for the same methanol production.

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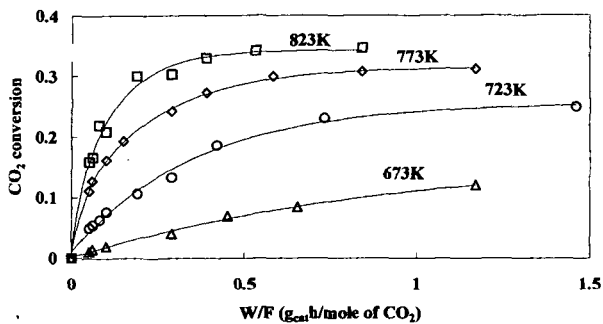


Figure 1. CO₂ conversion with reaction temperature over Fe₂O₃/Cr₂O₃ with the H₂/CO ratio of 1. The marks are experimental points; the lines are calculated values from the kinetic equation.

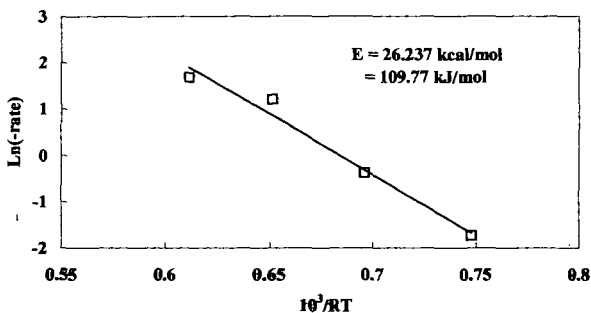
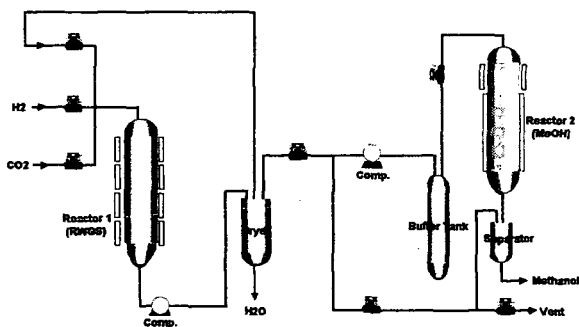


Figure 2. Arrhenius plot of specific activities for the continuous flow reaction of CO₂/H₂ of 1 over Fe₂O₃/Cr₂O₃ catalyst.



Scheme 1. CAMERE process diagram for MeOH of 5 kg/day from CO₂

Table 1. Comparison of the CAMERE process with a direct CO₂ hydrogenation.

Process	A1	R1	A2	R2	F1	F2	L1	L2	MeOH Yield	P
Direct CO ₂ Hydrogenation Process	-	-	1.0	0	14.3	11.7	1.47	0.57	16.04	11.7
	-	-	0.9481	1	24.3	20.4	2.23	0.94	26.32	10.2
	-	-	0.9243	2	32.5	27.2	2.78	1.22	34.12	9.08
	-	-	0.9100	3	38.9	32.8	3.21	1.44	40.31	8.20
	-	-	0.9003	4	44.3	37.5	3.56	1.62	45.35	7.49
	-	-	0.8930	5	48.8	41.4	3.85	1.77	49.54	6.90
	-	-	0.8874	6	52.7	44.8	4.10	1.90	53.10	6.40
	-	-	0.8829	7	56.2	47.8	4.31	2.00	56.16	5.98
	-	-	0.8790	8	59.2	50.5	4.49	2.10	58.82	5.61
CAMERE Process	0.3978	0	0.3978	0	12.2	8.66	1.30	1.10	30.80	8.66
	0.3978	0	0.4636	1	19.3	14.2	1.91	1.57	43.97	7.10
	0.3978	0	0.5050	2	24.2	18.4	2.32	1.86	51.92	6.13
	0.3978	0	0.5324	3	28.4	21.7	2.62	2.06	57.52	5.43
	0.3978	0	0.5514	4	31.7	24.4	2.85	2.21	61.81	4.89
	0.3978	0	0.5652	5	34.5	26.7	3.05	2.33	65.23	4.45
	0.3978	0	0.5753	6	36.7	28.6	3.21	2.43	68.05	4.08
	0.3978	0	0.5832	7	38.6	30.2	3.35	2.52	70.41	3.78
	0.3978	0	0.5893	8	40.3	31.6	3.46	2.59	72.43	3.52
	0.2906	1	0.2906	0	11.8	7.93	1.38	1.23	34.42	7.93
	0.2906	1	0.3487	1	18.1	12.6	2.00	1.74	48.69	6.29
	0.2906	1	0.3894	2	22.5	16.0	2.37	2.03	56.77	5.34
	0.2906	1	0.4188	3	25.6	18.7	2.64	2.22	62.16	4.69
	0.2906	1	0.4405	4	28.6	21.0	2.84	2.36	66.12	4.21
	0.2906	1	0.4569	5	30.9	22.9	3.00	2.47	69.22	3.83
	0.2906	1	0.4696	6	32.9	24.6	3.13	2.56	71.72	3.51
	0.2906	1	0.4795	7	34.5	26.0	3.24	2.64	73.81	3.25
	0.2906	1	0.4874	8	36.0	27.3	3.34	2.70	75.57	3.03

A1: CO₂ concentration in carbon oxide in the stream after RWReactor.

R1: Recycle ratio in the RWReactor.

A2: CO₂ concentration in carbon oxide in F1 stream.

R2: Recycle ratio in the methanol reactor.

F1: Feed gas for the methanol reactor (kgmol/h).

F2: Downstream gas in the methanol reactor (kgmol/h).

L1: Liquid product in the methanol reactor (kgmol/h).

L2: Methanol productivity (kgmol/h)

P: Purge gas (kg mol/h)

Methane Dry Reforming: Effects of Pressure and Promoters on Carbon Formation

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KEYWORDS: Dry reforming, Methane reforming, CO₂ utilization

INTRODUCTION

Natural gas, estimated to last well into the 21st Century, is composed mainly of methane and it is in direct competition with coal and oil as a fuel for the production of electricity. Use of natural gas which contains more hydrogen and fewer carbons than coal and oil will significantly reduce pollutants such as CO₂, SO_x, NO_x, and trace elements such as Sb, As, Be, Cl, Cd, Co, Cr, Pb, Hg, Mn, Ni, and Se.

In recent years there have been considerable efforts to develop catalysts for converting natural gas to fuels, fuel additives, and chemicals. Oxidative coupling of methane to ethane and ethylene and subsequent conversion of these chemicals to liquid fuel is one approach that has attracted great interest.^{1,2} A key to success for an economically viable process is the development of a catalyst that converts methane selectively into higher hydrocarbons, preferably ethylene, at a higher yield than current technology.

Early work at NETL demonstrated that it is possible to convert methane to higher hydrocarbons (C₂⁺ products) via oxidative coupling of methane, in which oxygen and methane were fed over a catalyst.^{3,4} Despite intensive efforts in this area, little progress has been achieved, mainly because the products of methane conversion, ethane and ethylene, are more reactive than methane and are converted to carbon oxides at a lower temperature compared to methane.⁶

The other method of producing fuels, fuel additives, and chemicals is via production of synthesis gas (a mixture of carbon monoxide and hydrogen) by steam reforming, partial oxidation, or dry reforming. Reforming methane combined with the water-gas shift reaction produces syngas suitable for synthesis of ammonia, methanol, Fischer Tropsch products, and chemicals. The cost of syngas production in converting natural gas to liquid fuels is more than 60% of the total cost. Therefore, reducing the cost of syngas will significantly affect the economics of gas to liquids processes. Most of these reactions are carried out catalytically and the development of new and novel catalysts is very important for utilization of natural gas, particularly for producing liquid fuels.

Recently many researchers have concentrated their efforts toward catalytic reforming of methane with carbon dioxide. This process can be very useful for converting thermal energy into chemical energy. For example, energy losses in combustion/gasification systems and in advanced gas turbines can be captured by reacting natural gas with the by-product of combustion (CO₂) over a catalyst producing syngas which can be converted into liquid fuels and chemicals, ultimately increasing the system efficiency. Although this concept has many environmental and economic incentives, unfortunately, there are no commercial processes for reforming of methane with CO₂. The main problem is that there are several carbon-forming reactions associated with this concept that deactivate the conventional steam reforming, nickel-based, catalysts. Nickel catalyzes carbon formation via hydrocarbon decomposition and CO disproportionation reactions, which greatly contributes to catalyst deactivation, specifically at higher pressures. Methane conversion decreases as the pressure increases due to water formation via the reverse water-gas shift reaction. Therefore, the challenge is to develop a catalyst which exhibits a high selectivity toward hydrogen and carbon monoxide without forming carbon. In this paper we report the preparation and testing of catalysts for dry reforming of methane to syngas at atmospheric and at higher pressures with and without promoters.

EXPERIMENTAL

Tungsten carbide catalyst was prepared as described in the U.S. patent 5321,161 by mixing 12 grams (0.03 mole) of tungsten hexachloride (WCl_6) with 8.6 grams (0.09 mole) of guanidine hydrochloride, $\text{HN}=\text{C}-(\text{NH}_2)_2\text{HCl}$.⁷ The mixture was heated from room temperature to 200 °C in two hours, held at this temperature for two hours, then the temperature was raised to 750 °C for seven and one-half hours and held at this temperature for two hours under nitrogen. Molybdenum carbide catalyst was prepared by temperature-programmed reduction of molybdenum oxide in a flow of 11.6% ethane or methane in hydrogen at a flow rate of 55 ml/min.

The nickel-based catalysts were prepared from water soluble nitrate solutions with proper metal ratios. A 0.3-m long quartz (1/2" stainless steel tube used for higher pressure) reactor tube (6.35-mm o.d., 4.0-mm i.d.) with a quartz thermocouple well was used as a fixed-bed reactor with 0.01-0.5 grams of catalyst (-28/+48 mesh) held in place by quartz wool. A thermal conductivity detector was used with a 1-m by 3.2-mm-o.d. stainless steel molecular sieve 5A column and a 3.66-m by 3.2-mm-o.d. stainless steel HayeSep C (80/100 mesh) column at isothermal oven temperatures of 120 and 50 °C, respectively. Argon was used as carrier gas at 20 ml/min.

RESULTS AND DISCUSSION

A series of carbide and Ni-based catalysts were prepared and tested at several reaction conditions for reaction of methane with CO_2 . Pure SiC was tested at 950 °C and no significant methane or CO_2 conversions were observed. Higher activity was obtained for pure tungsten carbide, which was tested at 650, 750, and 850 °C as shown in Figure 1. At temperatures of 650 and 750 °C methane and CO_2 conversions were less than 15% and H_2/CO ratio was about 0.2. A dramatic increase in CH_4 and CO_2 conversions plus a H_2/CO ratio of 1.1 was obtained at higher temperatures of 850 and 950 °C (not shown). Methane conversion of less than 15% and CO_2 conversion of less than 17% were obtained for commercially produced Mo_3C . However, when molybdenum carbide was prepared by temperature-programmed reduction of molybdenum (VI) oxide with a mixture of 11.6% ethane or methane in hydrogen, methane and CO_2 conversions of more than 90% were obtained at 950 °C and 1.0 atm. A lower H_2/CO was obtained at lower temperatures. Molybdenum carbide catalyst was tested for 16 hrs and the results are shown in Figure 2. Higher catalytic activity was observed for the catalyst prepared with ethane mixture compared to that prepared with methane mixture. Molybdenum carbide supported on TiO_2 was prepared by mixing MoO_3 with TiO_2 in an ethyl alcohol slurry. The dried mixture was reacted with 11.6 vol.% ethane in hydrogen to form carbide. About 90% of methane and 100% of CO_2 were converted to hydrogen and CO with a ratio of 1.0 and the test continued for 2.5 hours at 900 °C without deactivation or forming significant amounts of carbon.

We also tested two commercial nickel-based catalysts. The results for R-67 are shown in Figure 3. Similar results were obtained for G-56B catalyst. Although these catalysts showed a similar activity and selectivity compared to carbide and noble metal catalysts at temperatures higher than 850 °C, none of the experiments lasted more than five hours because a significant amount of carbon formed on the catalyst bed plugging the reactor tube. Zero activity in Figure 3 means that there was no flow due to carbon formation that plugged the reactor. We prepared a series of Ni-based catalysts promoted with alkali and alkali earth metals which were tested for more than 360 hours at 850 °C and at atmospheric pressure. The amount of carbon deposition was reduced significantly due to addition of alkali and alkali earth metals. The promoted catalyst was tested at 7 and 13 atm for 6 hours. Methane and CO_2 conversions decreased as the pressure increased.

CONCLUSIONS

A series of carbide and Ni-based catalysts were prepared and tested at several reaction conditions for reaction of methane with CO_2 . The Ni-based and carbide catalysts were very active and selective for producing syngas. However, a significant amount of carbon formed on the commercial Ni-based catalysts, plugging the reactor after five hours on stream. The amount of carbon deposition was reduced significantly due to addition alkali and alkali earth metals. Methane conversion decreased as the pressure increased, due to water formation via the reverse

water-gas shift reaction. Molybdenum carbide catalyst appeared to be stable for ten hours, at atmospheric pressure, and after that methane and CO₂ conversions slowly decreased due to oxidation of molybdenum carbide to molybdenum oxide.

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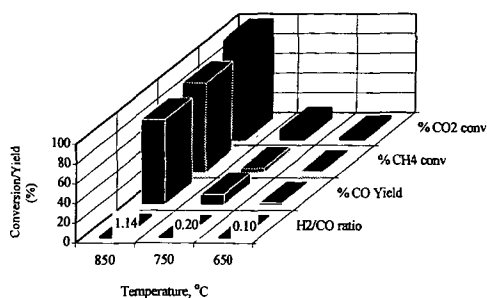


Figure 1. Effect of temperature on dry reforming of methane over Tungsten carbide, $\text{CH}_4/\text{CO}_2=1.15$, GHSV = $5040 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$

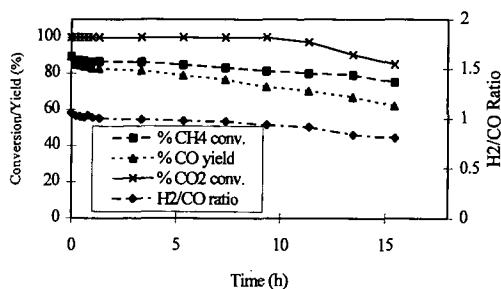


Figure 2. Dry reforming of methane over molybdenum carbide, $\text{CH}_4/\text{CO}_2=1.16$, GHSV = $5040 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ at 850°C

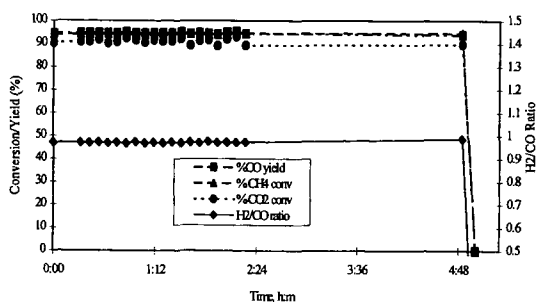


Figure 3. Dry reforming of methane over Ni-based catalyst (R-67), CH_4/CO_2 ratio = 1.1, GHSV = $5040 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, at 750°C , no flow after 5 hours.

CONVERTING OF CARBON DIOXIDE INTO MORE VALUABLE CHEMICALS USING CATALYTIC PLASMAS

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Key words: carbon dioxide, plasma, alkene, oxygenate

ABSTRACT

Experiment has confirmed that the CO_2 plasmas can generate a plentiful of active oxygen species and other active plasma species for further reaction with other reactants, like methane, low alkanes and others. These reactions leads to a formation of more valuable chemicals, like ethylene, propylene and oxygenates. The characteristics of CO_2 plasma reactions have been addressed therefore in this paper. To be our surprised, the experiment has shown that the CO_2 plasma is an excellent "catalyst" for the conversion of low alkanes to alkenes (esp., ethylene and propylene). To the knowledge of authors, this is the first report of this kind of experiments that could lead to a novel method for the utilization of CO_2 and low alkanes. The present yield of alkenes achieved has been competitive to that from the conventional catalytic dehydrogenation of low alkanes.

INTRODUCTION

Any success in research and development of a feasible utilization of carbon dioxide will signify the attainment of objectives of slowing down a build-up of greenhouse gases in the atmosphere and better carbon resource utilization. Due to the difficulty in the utilization of carbon dioxide via the conventional catalysis, plasma approaches for the CO_2 utilization have been paid more and more attentions^[1-10]. Within these plasma CO_2 utilization, an indirect utilization (via syngas) and a direct utilization have been investigated^[1]. The plasma CO_2 utilization is being demonstrated to be an efficient method. In addition, the plasma flue gas treatment has become an industrialized operation. If more valuable chemicals can be directly produced from such plasma CO_2 utilization, the CO_2 emission control will become compensable. In this presentation, the recent progresses in converting of CO_2 into more valuable chemicals using dielectric-barrier discharge (DBD) plasmas has been reported. It has been found that CO_2 is a very good reactant within gas discharge plasmas for organic synthesis.

EXPERIMENTAL

The DBD is one of non-thermal plasma phenomena, which has been considered very promising for organic chemical reactions because of its non-equilibrium properties, low input power requirement and its capacity to induce physical and chemical reactions within gases at relatively low gas temperatures^[1,4,6]. Figure 1 illustrates the reactor system. The feed gas flow is subjected to the action of the DBD in an annular gap formed between an outer stainless steel tube maintained at constant temperature and an inner quartz tube. The radial width of the discharge space was 1 mm, its length 50mm ~ 300 mm. This reactor system is very similar to the DBD reactor for methane conversion described elsewhere^[4,6]. All the experiments were conducted at atmospheric pressure. The feed and exhaust gases were analyzed by gas chromatograph (MTI M200H and HP 4890) with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The exhaust gas from the reactor was first introduced into a condenser to separate

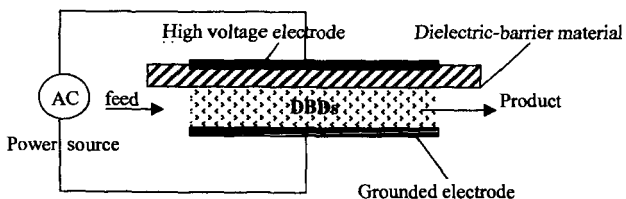


Figure 1 Schematically representative of DBD reactor system

the condensable product from the gas. The power is applied by a high voltage generator working at about 25 kHz. The power can be varied by adjusting the voltage amplitude which causes a slight change of frequency. The voltage and current measurements were conducted using a high voltage probe (Tektronix P6015) and a current probe (Tektronix CT-2) with a digital oscilloscope (Tektronix TDS 210).

RESULTS

We have previously reported a direct liquid fuel synthesis from methane and carbon dioxide via DBDs.^{1,4} During this liquid fuel synthesis, the formation of ethylene and propylene, that is very important chemicals, have been observed. Upon the feed ratio of carbon dioxide/methane, a significant amount of oxygenates has also been detected. Figure 2 shows the effect of feed ratio of CO_2/CH_4 on the conversions and selectivities. It is clear that a lower CO_2/CH_4 feed ratio leads to a higher selectivity of ethylene and propylene. The highest selectivity of ethylene and propylene presents under the feed of pure methane. However, the methane conversion with the pure methane feed is low. The addition of carbon dioxide significantly increases the methane conversion but reduces the selectivity of alkenes. A mixture of oxygenates including methanol, DME, formaldehyde and so on has thereby been produced. Table 1 shows a summary of selectivities based upon the oxygen balance. The higher CO_2 amount in the feed will induce a larger selectivity of oxygenates. Further investigations are being conducted to improve the selectivity of desired oxygenate, e.g. methanol. To get a higher selectivity of alkenes, a lower CO_2 feed amount is suggested. In addition, the use of zeolite within the DBDs and changes in other plasma reaction condition can increase the selectivity of alkenes. We will report it in the near future.

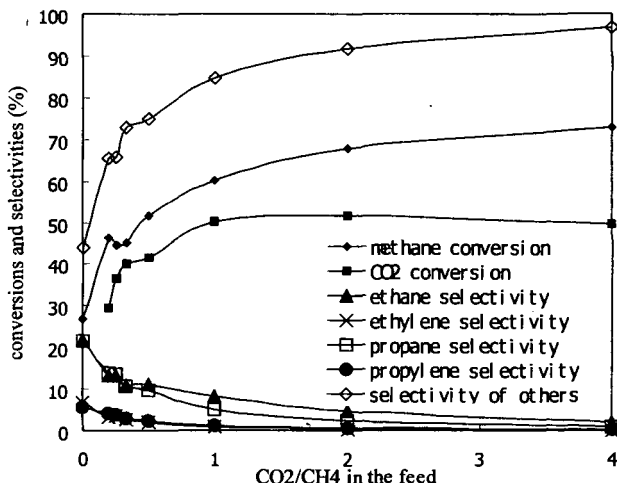
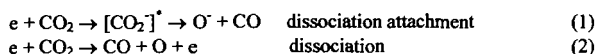


Figure 1 Effect of CO_2/CH_4 feed ratio on the selectivities based on the carbon balance (input power: 500w; feed rate: 150 ml/min; gas temperature: 150°C; gas pressure: 1 bar)

Table 1. Effect of CO_2/CH_4 feed ratio on the selectivities based on the oxygen balance

CO ₂ /CH ₄	Selectivity (%)		
	CO	H ₂ O	Oxygenates
0			
1/4	61.5	24.2	14.3
1/3	59.9	21.1	19.1
1/2	64.1	22.3	13.5
1/1	47.8	15.7	36.4
2/1	43.3	12.7	44.0
4/1	41.1	9.2	49.7
0	100.0		

It is generally accepted that the ethylene and propylene are from the secondary reactions of ethane and propane. The initiation reactions are thought to be the DBD-induced plasma dissociation of CO₂ and CH₄ to generate various radicals, like methyl, ethyl, propyl radicals and so on. A hydrocarbon chain growth reaction is thereby induced to produce ethane, propane and other higher hydrocarbons. Especially, the DBDs can generate a significant amount of active oxygen species from the following plasma CO₂ reactions:



The oxygen species O and O⁺ are being of excited state or metastable state. These plasma species are very active for the dehydrogenation of alkanes and lead to the formation of ethylene and propylene. Experimental investigations have confirmed there are at least two kind of oxygen species produced in the DBDs from carbon dioxide: one leads to the formation of alkenes and oxygenated hydrocarbons and the other induces the complete oxidation of hydrocarbons. A comparative investigation has been conducted to study the decomposition of pure carbon dioxide. It has been found that the plasma decomposition of pure carbon dioxide in some of our reactor designs is higher than that of carbon dioxide and methane or other alkanes (ethane and propane conducted in this investigation) at the same reactive conditions. For example, a CO₂ conversion is 18% with pure CO₂ feed, while the CO₂ conversion reduces to 10% with a mixture feed of carbon dioxide and low alkanes. It can be considered that the CO₂ plasma could be a good catalyst for the conversion of alkanes. A high conversion has been achieved. The challenge, however, is that plasma is a complex mixture of electrons, radicals, ions, photons and others. Especially, the products (alkenes or oxygenates) from plasma CO₂ utilization using alkanes as hydrogen sources are easily to be destroyed by plasma species. It is very necessary to exploit how to control the activity of each plasma species. A special "quenching" has been successfully applied in our investigation on the conversion of low alkanes (ethane and propane) with CO₂ plasma and a selective production of alkenes has been achieved. The high selectivity of alkenes (as high as 80%) can be competitive to the conventional catalytic conversion of low alkanes. Table 2 shows a result of effect of CO₂/C₃H₈ feed ratio on the selectivity of propylene. The products from this DBD conversion of carbon dioxide and propane only contain propylene, water, carbon monoxide and a small amount of iso-butane. Compared to hundreds of components produced^[4], this is a significant improvement in the organic synthesis via non-thermal plasmas and could lead to a practical application of plasma synthesis of more valuable chemicals from low alkanes and carbon dioxide.

Table 2 Effect of carbon dioxide/propane ratio in the feed on the selectivities

CO ₂ /C ₃ H ₈	conversions (%)		selectivities (%)		
	CO ₂	C ₃ H ₈	C ₃ H ₆	CO	iso-C ₄ H ₁₀
1/3	15.6	7.7	73.4	17.6	8.9
1/2	11.0	7.3	77.2	16.3	6.5
1/1	10.9	9.2	72.9	19.7	7.4

CONCLUSION

The potential of the utilization of CO₂ plasma has been demonstrated in this investigation. Due to the low price of present oil market, the synthesis of liquid fuel^[4] from methane and carbon dioxide would not be a good option. The production of more valuable chemicals, like ethylene and propylene, is a better choice for the utilization of carbon dioxide, together with the utilization of low alkanes, especially methane, ethane and propane. It can be considered this as an important innovative alternative technology to produce ethylene and propylene.

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DEVELOPING INNOVATIVE SYNTHETIC TECHNOLOGIES OF INDUSTRIAL RELEVANCE BASED ON CARBON DIOXIDE AS RAW MATERIAL

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Abstract: The reduction of carbon dioxide emission requires the implementation of several convergent technologies in different production sectors. The chemical industry can contribute to the issue with innovative synthetic technologies, that implement the principles of atom-economy, dematerialisation, energy saving, and raw material diversification with carbon recycling. The innovative synthetic methodologies merge the issues of avoiding the production of CO₂ and carbon recycling, through carbon dioxide utilisation.

In this paper, some options will be discussed, namely the synthesis of carboxylic acids, organic carbonates, and carbamates/isocyanates. The synthesis of methanol from CO₂ and CO will be compared.

Keywords: carbon dioxide, innovative syntheses

Introduction

The implementation of innovative synthetic technologies based on CO₂ can considerably contribute to the reduction of carbon dioxide emission. The avoided amount is not simply represented by the amount of CO₂ fixed. As we have already discussed, the assessment of the exact amount of avoided CO₂ requires an integrated approach which takes in consideration several parameters, as shown in Scheme 1.¹

Amount of CO₂ fixed per t reacted

$$1 - Y + Z$$

$$Y = \sum (e_r, e_{oc}, e_{pi}, e_{wt}, \dots)$$

$$Z = \sum (e_{sc}, e_{vr}, e_{vpi}, e_{vwt}, \dots)$$

as CO₂ equivalent

**e_r* = energy of reaction; *e_{oc}* = energy of other reagents; *e_{pi}* = energy of purification; *e_{wt}* = energy of waste treatment; *e_{sc}* = energy of substituted reagents and solvents; *e_{vr}* = variation of the reaction energy with respect to the synthesis that does not use CO₂; *e_{vwt}* = variation of waste treatment energy; *e_{vpi}* = variation of energy of purification*

Scheme 1.

The exact evaluation of each parameter can be only made by using a methodology like Life Cycle Analysis, LCA,² that demands an exhaustive basis of process-data, including emission, energy and mass data.²

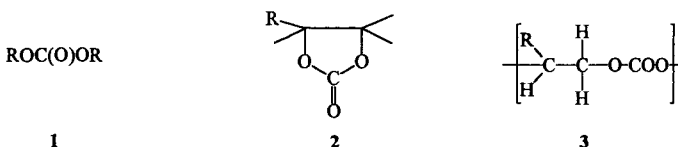
New synthetic methodologies that implement the principles of atom economy, solvent shift, waste minimisation at source, use of less noxious materials and carbon recycling, contribute to CO₂ reduction in many different ways, that cannot be discovered and quantified by simply looking at the stoichiometry of a reaction.

The target compounds considered in this paper are: organic carbonates, carboxylic acids (long-chain aliphatic, or mono- and di-carboxylic aromatic), carbamates and isocyanates. They are today prepared using quite energy- and material-intensive synthetic methodologies, while could be synthesised by using more eco-efficient and economic pathways, including those based on carbon dioxide.

The last section of the paper will be devoted to the analysis of methanol synthesis from CO₂ and CO.

Discussion

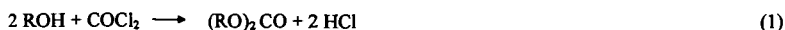
Monomeric (linear 1 and cyclic 2) and polymeric organic carbonates 3 have a market of ca. 1.8



Mt/y, bisphenol-A-polycarbonate being by far the largest commercialised product.

However, the large majority of the production of non polymeric carbonates does not reach the market, as they have a captive use as solvents and internal commodities.

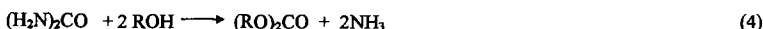
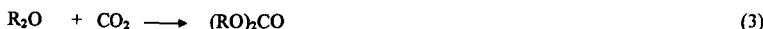
The large majority of the products is produced by the old phosgenation of alcohols, (Eq. 1)



a technology that has a positive aspect in the high reactivity of phosgene, and black spots in the high energy requirement for the synthesis of chlorine, the limitation to the transport of phosgene, the safety measures required for the use of phosgene, the chloride and halogenated solvents end-production. These aspects may be a barrier to further enlargement of the technology exploitation and to a many-purpose use. As a matter of facts, the limitation to the transport of phosgene, concentrates its use at its production site and has encouraged the building up of small-medium-units that can be mounted at the customer site. This is not the solution to problems.

Alternative syntheses are now on stream based on the oxidative-carbonylation of methanol (ENIChem and Ube processes).

The synthetic approaches proposed in this paper consider the reaction of alcohols (Eq. 2), ethers (Eq. 3), or urea with carbon dioxide (Eq. 4), the reaction of ketals with carbon dioxide and alcohols (Eq. 5), and the oxidative-carboxylation of olefins (Eq. 6).



All these syntheses are characterised by a high atom efficiency. The only by-product is water.

This is true also for reaction 5, in which the ketone and glycol can be reconverted into the ketal, that is used as promoter of the reaction of carbon dioxide with alcohol.

Reactions 3 and 5 avoid the water formation in the reaction medium, that can be crucial for equilibrium shift.

Processes based on reactions 2-6 are more eco-efficient than existing ones and are characterised by an atom economy close to 100%. The phosgene based technology (Eq. 1), quite attractive for the easy reaction conditions and high yield, as reported above, has weak points in the fact that it is energy intensive and produces undesired chloride ions and waste chlorinated solvents. These attributes may not guarantee that phosgenation will continue to be the leader technology in the future and will be able to cover the demand of carbonates that is expanding, especially for the production of speciality chemicals and DMC.

The use of carbon dioxide is a better option with respect to both phosgene and carbon monoxide. CO_2 can be recovered from industrial plants, responding, thus, to the principle of recovery and recycling, and to the international agreement of reducing greenhouse gases emission.

This goal is met not only for the recycled fraction of carbon dioxide, but also, and essentially, for the avoided use of natural resources, necessary for the synthesis of carbon monoxide or phosgene, and, the reduced production of waste.

A preliminary Life Cycle Assessment, LCA, study performed considering reactions 1, 2 and 4 has clearly shown that reaction 1 has an impact factor much higher than reactions 4 and 2, (Fig. 1) the key steps responsible for such high impact being the energy required for the synthesis of chlorine, and the production of chloride.

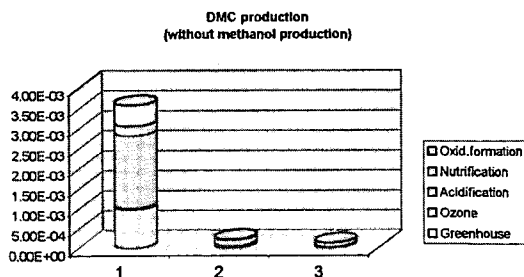
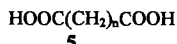
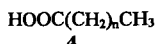


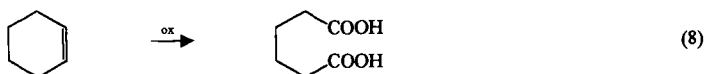
Figure 1. LCA of alternative synthetic pathways for the synthesis of DMC.

- 1: DMC from phosgene and methanol; 2: DMC from urea and methanol;
- 3: DMC from methanol and CO_2 .

Long chain mono- and di-carboxylic acids, **4** and **5** respectively, are high quality products with a major use in polymer chemistry.

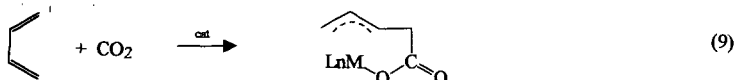


Presently, the latter are synthesised by oxidation of di-alcohols (Eq. 7) or cyclic alkanes/alkenes (Eq. 8) by oxidative ring cleavage with formation of the two carboxylic functionalities.

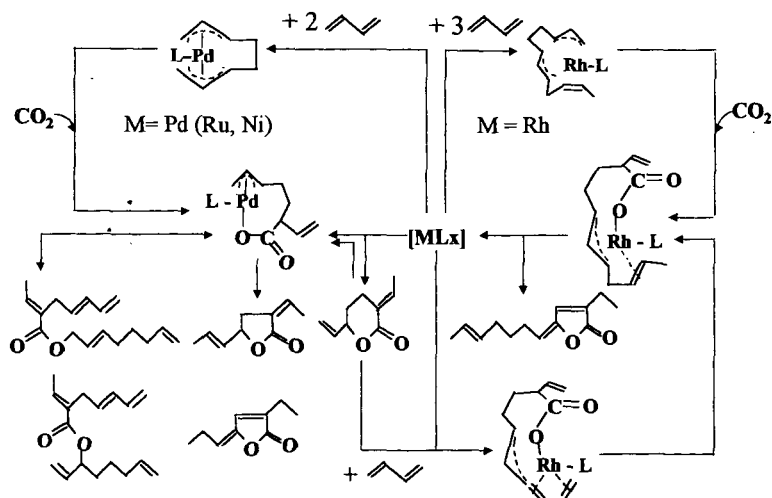


Such processes are neither atom-efficient nor selective. Such non-convergent and destructive synthetic approach, with high waste production, is a major draw-back that cancels-out the advantages of the use of heterogeneous catalysts. An analogous situation exists for long chain mono-carboxylic acids that find a wide application as additives, and in the production of surfactants.

The use of dienes and carbon dioxide as substrates (Eq. 9) brings in the great advantages of atom-economy and selectivity.⁴



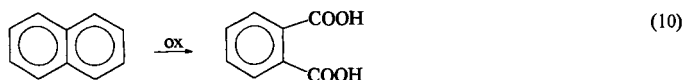
Such synthetic approaches are now known for lactones and can be also used for both the synthesis of either di- or mono-carboxylic acids, by changing the catalyst and controlling the reaction conditions. C-5 or C-9 mono-carboxylic or C-10 di-carboxylic acids can be prepared in mild conditions from butadiene and carbon dioxide. Longer chains can be also built up, according to the metal used. (Scheme 2)



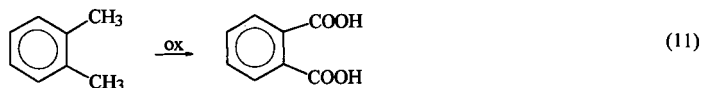
Scheme 2. Metal catalysis in butadiene- CO_2 chemistry.

The reaction is controlled through the use of specific ligands on the metal centre.

Aromatic mono- and di-carboxylic acids are prepared using drastic oxidation reactions (Eq. 10) with low atom efficiency.

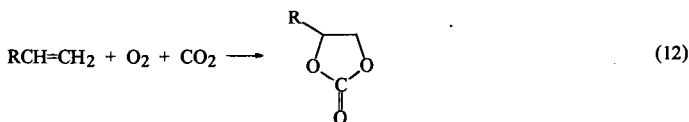


The side chain oxidation of alkyl-aromatic compounds (Eq. 11), which may yield different type of oxygenated organic chemicals, pertains to a large number of industrial intermediates addressed to the manufacture of plastics, fibres, pharmaceuticals, agrochemicals, etc.



At present, these oxidation reaction, namely to obtain the correspondent aromatic acids, are commercially carried out both in the gas and liquid phase. Gas phase processes adopt fixed or fluidised-bed, on V_2O_5 based catalysts, with air as oxidant, at temperatures ranging from 350 to 550 °C; liquid phase oxidation routes, usually with metal salt catalysts dissolved, adopt milder reaction conditions, 110-180 °C, pressure up to 2 MPa. Soluble acetates or naphthenates of Co, Mn, or Mo are generally used with bromine-based co-catalysts. Carboxylic acids, mainly acetic acid, are added as solvents. Benzoic and phthalic acids or anhydride production, accounting for more than 16 Mt/y, rely on these current technologies, by processes with relevant objections for what concerns the formation of polluting effluents, the use of corrosive conditions due to the aggressivity of the reaction medium employed, the low or moderate selectivity in the synthesis of partially oxygenated intermediates, such as ketones and aldehydes, the low or moderate conversions, due to the necessity to maintain the reaction system outside the explosion limits. In addition some of these processes are not continuous.

The oxidation of olefins with dioxygen is a process that has found a seldom exploitation like in the synthesis of ethylene oxide.³ In most other cases, peroxides are used as oxidants with high costs. The oxidation of olefins with dioxygen and CO_2 (Eq. 12) may bring in positive results.⁶



The use of sc- CO_2 may add some more benefits for what concerns critical aspects difficult to drive in solution, namely: the control of the reaction selectivity (one- or two-oxygen transfer to the substrate), yield, working conditions, eventual radical life-time control.

Moreover, the use of sc- CO_2 offers a unique opportunity of using carbon dioxide as solvent and reagent.

Another area of application for carbon dioxide is the use in the synthesis of methanol that is actually synthesised from CO/H_2 mixtures. (Eq. 13) Methanol may have a large market as fuel and chemical and its synthesis from carbon dioxide attracts the attention and interest of several research groups around the world in order to define the potential.



The use of carbon dioxide (Eq. 14) has as major draw-back the higher consumption of dihydrogen with respect to CO.



However, higher selectivity and better yields may counterbalance such apparent negative point. We have performed a LCA study of the possible synthetic methodologies of methanol⁷ and found that the most eco-efficient synthesis is based on the use of a mixture of $\text{CO}:\text{CO}_2=2:1$.

Conclusions

All the synthetic methodologies described above respond to the enviro-economics principles. They are characterised by a great level of innovation and promote the corporate image of the

chemical industry as they couple the reduction of carbon dioxide emission and waste minimisation at source with possible recycling of carbon. Their implementation is on a time scale short to medium, with great benefits for the chemical industry.

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